Polymerization

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Control of a Living Radical Polymerization of Methacrylates by Light**

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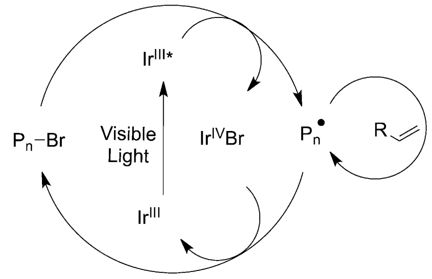
The ability to precisely control molecular weight and molecular weight distributions, as well as gain sequence and architecture control in polymer synthesis is of considerable importance and has greatly impacted the advancement of science and technology.[1] Indeed, the development of controlled living polymerization methods has profoundly changed polymer research with strategies, such as nitroxide-mediated radical polymerization (NMP),[2] atom transfer radical polymerization (ATRP),[3] and reversible addition fragmentation chain transfer polymerization (RAFT),[4] allowing the facile synthesis of well-defined polymers that are diverse in both their structure and function.

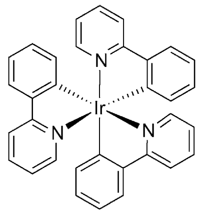
Recently there has been an effort to dramatically increase the scope of living radical polymerization through the development of strategies to regulate the activation and deactivation steps by using an external stimulus.[5–7] Arguably, the most successful strategy that controls both the initiation and growth steps has been the recent work of Matyjaszewski and co-workers who exploited the unique aspects of electrochemistry to control the ratio of activator to deactivator in ATRP.[5] By selective targeting of redox-active catalytic species, the polymerization reaction could be turned "on" and "off" by adjusting parameters such as applied current, potential, and total charge passed.

As with traditional radical polymerization, the most robust and widely used form of regulation is through photopolymerization, which is a pervasive procedure in both academia and industry.[8] The ability to develop a photocontrolled living radical polymerization would, therefore, represent a significant breakthrough. Interestingly, one of the earliest attempts to develop a living radical polymerization involved iniferter polymerization using a dithiocarbamate under UV irradiation.[9] However, the procedure was intrinsically limited and poor control and broad molecular weight distributions were obtained. Subsequently, photoinitiation of ATRP,[7] NMP,[10–13] and RAFT[14–17] polymerizations have been developed, though in all cases only the initiation step was photocontrolled and all subsequent growth steps could not be photoregulated. As a result, the development of a highly responsive photocontrolled living radical procedure, which affords control over the chain growth process, is both a major opportunity as well as challenge for the future of living polymerizations.

The key to addressing this challenge was recent work by the research groups of Macmillan,[18] Yoon,[19] Stephenson,[20] and others[21] who have exploited the power of photoredox catalysts for organic transformations that are mediated by visible light.[22–25] We envisaged that the unique properties of these photoredox catalysts would allow for the development of a highly responsive photocontrolled living radical polymerization. Our proposed mechanism for this process is shown in Scheme 1. The *fac*-[Ir(ppy)$_3$] (**1**, Figure 1), a commercially available complex utilized previously by Macmillan and co-workers, has been shown to absorb visible light to afford *fac*-[Ir(ppy)$_3$]*.[26,27] We anticipated that this excited Ir^{III}* species would reduce an alkyl bromide initiator to give the desired alkyl radical, which could initiate polymerization of the monomer. The key to this process is that the highly oxidizing Ir^{IV} complex could then react with the propagating radical to afford the initial Ir^{III} complex in the ground state, as well as a dormant polymer chain with a bromo end group. Having regenerated the starting Ir^{III} complex, homolysis of



Scheme 1. Proposed mechanism of a visible-light-mediated living radical polymerization using an Ir-based photoredox catalyst. P$_n$ = polymer chain.



fac-[Ir(ppy)$_3$] (**1**)

Figure 1. The photoredox catalyst *fac*-[Ir(ppy)$_3$] (ppy = 2-pyridylphenyl).

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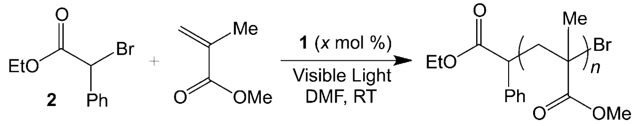
the C−Br bond, addition of monomer to the radical chain end and recapping with bromide can occur with the overall cyclic process being mediated by visible light.[28,29] Significantly, this would result in a photochemically controlled, living ATRP-like process. However, the most advantageous aspect of this type of system, and what sets it apart from traditional Cu-mediated ATRP methods, is the ability to reversibly activate or deactivate the polymerization with visible light. Specifically, when light is removed from this reaction no $\mathrm{Ir^{III}}$* will be present, and the polymerization will rest at the dormant, and stable, bromo chain-terminated species. Further, upon reexposure to visible light, $\mathrm{Ir^{III}}$* will be formed, reactivating the polymerization allowing for true control over polymer structure and architecture.

Initially, the polymerization of methyl methacrylate (MMA) was examined by using the Ir complex **1** as the catalyst, ethyl-α-bromophenylacetate (**2**) as the initiator, and a 50 W fluorescent lamp as the light source. In keeping with the simple, user friendly nature of traditional ATRP, complex **1** was selected for preliminary studies owing to its stability, highly reducing nature, and commercial availability.[30] Encouragingly, initial results employing 0.2 mol% catalyst did afford polymer; however, the reaction displayed little to no control, with a M_w/M_n value of 2.76 (Table 1, entry 1). We reasoned that our photoredox catalyst **1** was only acting as an initiator in this reaction, and to gain control over this system the radical concentrations needed to be lowered, which could be achieved by simply reducing the catalyst loading. In support of this hypothesis, it was found that significantly decreasing the loading of **1** to 0.005 mol% led to excellent control over the polymerization with a molecular weight distribution of 1.25 being obtained (Table 1, entry 2); this low catalyst loading is a highly desirable feature. Further, under the optimized reaction conditions subsequent polymerizations demonstrated that the molecular weight of the polymer could be efficiently controlled by changing the monomer/initiator ratio with close agreement between the experimental and theoretical molecular weights (Table 1, entries 2–5).

Table 1: Molecular weight and polydispersities for the visible-light-mediated polymerization of methyl methacrylate using $[\mathrm{Ir(ppy)_3}]$.[a]



Entry	1 [mol%]	M_n (experimental) [kg mol^{-1}]	M_n (theoretical) [kg mol^{-1}]	M_w/M_n
1	0.2	40.3	25.0	2.76
2	0.005	22.9	20.0	1.25
3	0.005	12.0	11.0	1.23
4	0.005	6.3	5.6	1.19
5	0.005	2.9	2.5	1.22
6	0	0	–	–
7[b]	0.005	0	–	–

[a] Reaction conditions: MMA (1 equiv), **1** (0–0.2 mol%), and **2** (0.002–0.20 equiv) in DMF (0.37 mL mmol^{-1} of MMA) at room temperature with irradiation from a 50 W fluorescent lamp (M_n = number average molecular weight; M_w = weight average molecular weight). [b] The reaction was run in the absence of visible light.

To confirm the proposed mechanism, control polymerizations were conducted without added catalyst or in the absence of light, and in both examples no reaction was observed (Table 1, entries 6 and 7). Additional supporting evidence was obtained through fluorescence studies.[26] When **1** was combined with various concentrations of MMA, no change in the fluorescence of the Ir complex was detected. However, when the same experiment was performed with the initiator, ethyl-α-bromophenylacetate, a concentration-dependent fluorescence quenching was observed. These results suggest that the excited $\mathrm{Ir^{III}}$* complex is undergoing a redox process with the initiator and not reacting with the monomer (see the Supporting Information for more details).

The lack of any reaction in the absence of visible light suggests that a true "on"–"off" living photopolymerization system could be developed. To demonstrate this possibility, monomer, initiator, and catalyst were initially combined in the absence of light and after one hour no polymerization was observed. The reaction was then exposed to visible light for two hours at room temperature, which resulted in approximately 15% monomer conversion. In demonstrating true temporal control, removal of the light source stops the polymerization immediately and no conversion was observed during the dark period (1 hour). Exposure to light for a second two-hour period "turns" the polymerization back on and this "on"/"off" cycle can be repeated numerous times without observable reaction in the absence of irradiation (Figure 2a). These results demonstrate that this system is highly responsive to our external stimulus and when light is removed from the system polymerization stops almost immediately. This high degree of temporal control illustrates the efficient nature of the *fac*-$[\mathrm{Ir(ppy)_3}]$ catalyst for reversible activation and deactivation of the bromo chain end.

To clearly demonstrate that existing chain ends are reactivated during these "on"/"off" cycles with no new chains being initiated during the polymerization, plots of $\ln([M]_0/[M]_t)$ versus total exposure time (Figure 2b), and M_n versus conversion (Figure 2c) both gave linear relationships. Significantly, this data proves that when the light is turned off and polymerization stops, termination of the chain ends is not occurring and in the absence of light, the dormant species is the stable bromo chain end. In analogy with traditional ATRP, when these dormant chain ends are reexposed to light in the presence of the iridium catalyst, efficient reactivation of the chain ends is achieved. These features provide compelling evidence that this process is a photocontrolled living radical polymerization, which is highly responsive to visible light as an external stimulus.[31]

To further probe the living nature of this system, as well as provide additional evidence for the presence of active bromo groups at the chain ends, block copolymers were prepared using sequential photocontrolled living radical procedures (Figure 3). Initially, irradiation of a mixture of methyl methacrylate and the initiator **2** in the presence of the iridium photocatalyst **1** (0.005 mol%) afforded a well-defined PMMA derivative, **3**, with controlled molecular weight and

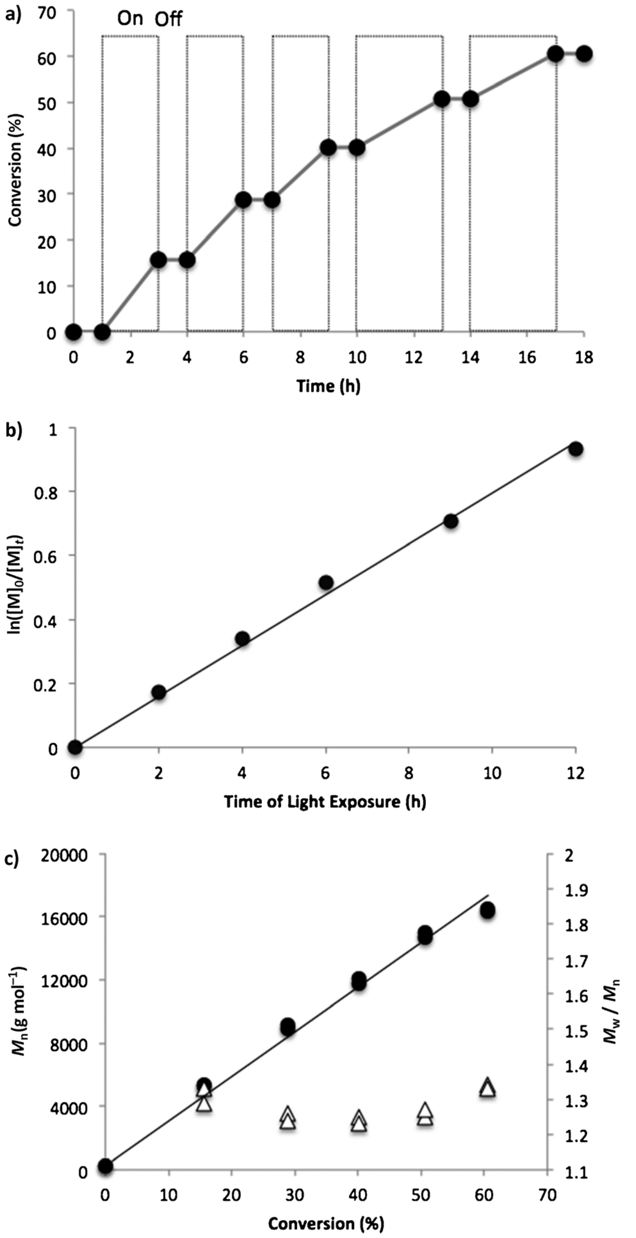


Figure 2. Polymerization of MMA using catalyst **1** while cycling the reaction's exposure to visible light. a) Conversion vs. time; b) time of light exposure vs. ln([M]$_0$/[M]$_t$), with [M]$_0$ and [M]$_t$ being the concentrations of monomers at time points zero and t, respectively; c) conversion vs. M_n (●) and conversion vs. M_w/M_n (Δ).

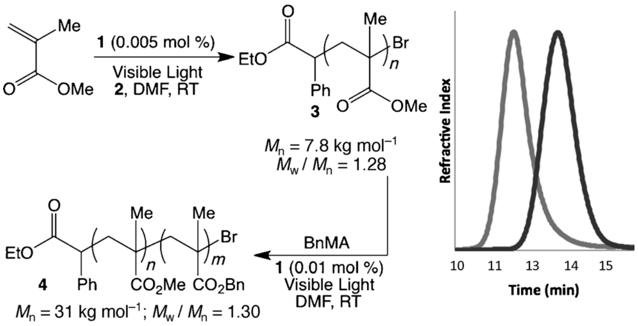


Figure 3. Synthesis of a poly(methyl methacrylate)-*b*-(benzyl methacrylate) diblock copolymer. Size exclusion chromatogram with the gray and black traces corresponding to **4** and **3**, respectively, is shown on the right.

Table 2: Synthesis of random copolymers and the homopolymer of methacrylic acid (MAA).[a]

Entry	MAA:BnMA	M_n [kg mol^{-1}]	M_w/M_n
1	10:90	21	1.24
2	20:80	22	1.36
3	100:0	28	1.61

[a] Reaction conditions: MAA (0.1–1.0 equiv), BnMA (0–0.90 equiv), **1** (0.005–0.13 mol%), and **2** (0.004 equiv) in DMF (0.37 mL mmol^{-1} of monomer) at room temperature with irradiation from a 50 W fluorescent lamp; for characterization the polymers were methylated after polymerization with TMSCHN$_2$ (TMS = trimethylsilyl) to give the methyl ester.

low polydispersity. Use of **3** as a macroinitiator in the polymerization of benzyl methacrylate and in this case, 0.01 mol% of **1**, proved to be a well-behaved process leading to the desired poly(methyl methacrylate)-*b*-(benzyl methacrylate) diblock copolymer **4**, with size exclusion chromatography showing little or no starting macroinitiator (Figure 3). This efficient block copolymer formation further illustrates that minimal termination is occurring during the polymerization process.

A major difference between the reported photocontrolled living radical polymerization and traditional ATRP procedures is the stability of the catalyst, with the Ir-based system being extremely tolerant to a variety of functional groups. To demonstrate this added versatility, the synthesis of homopolymers of methacrylic acid (MAA), which is notoriously difficult to polymerize under ATRP conditions, and random copolymers of MAA and benzyl methacrylate (BnMA) were examined. Under standard conditions and at 10% incorporation of MAA, excellent control over molecular weight and a low polydispersity were observed. Moreover, the polydispersity increased only slightly with higher MAA content (Table 2). These polymerizations in the presence of a free carboxylic acid exemplify the robust nature of our Ir-based catalyst **1**. Moreover, this excellent functional-group tolerance is an additional advantage over a traditional Cu-based ATRP process.

In summary, we have developed a new controlled living radical polymerization that displays an unprecedented response to activation and deactivation of polymerization through external visible light stimulation. The advantages of this approach lie in its highly responsive nature, facile reaction setup, use of only ppm levels of catalyst, and excellent functional group tolerance. In analogy with the pervasive nature of traditional photopolymerization and ATRP procedures, this photocontrolled living radical polymerization offers a versatile platform for the preparation of functional materials with applications in sustainability, electronics, and health.

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